



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C10M 127/06, 161/00 // (C10M 161:00 C10M 127:04, 127:06, 133:52 C10M 143:12, 143:10) C10N 30:04, 40:00	A1	(11) International Publication Number: WO 89/ 00186
(21) International Application Number: PCT/US88/02045 (22) International Filing Date: 14 June 1988 (14.06.88) (31) Priority Application Number: 071,003 (32) Priority Date: 8 July 1987 (08.07.87) (33) Priority Country: US (71) Applicant: THE LUBRIZOL CORPORATION [US/ US]; 29400 Lakeland Boulevard, Wickliffe, OH 44092 (US). (72) Inventor: MURPHY, John, P. ; 37508 Grove Avenue, Willoughby, OH 44092 (US). (74) Agents: FISCHER, Joseph, P. et al.; The Lubrizol Cor- poration, 29400 Lakeland Boulevard, Wickliffe, OH 44092 (US).		(43) International Publication Date: 12 January 1989 (12.01.89)
(81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), CH (European patent), DE (Euro- pean patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European pa- tent), NL (European patent), SE (European patent).		Published <i>With international search report.</i>
(54) Title: ALIPHATIC HYDROCARBON SUBSTITUTED AROMATIC HYDROCARBONS TO CONTROL BLACK SLUDGE IN LUBRICANTS		
(57) Abstract <p>A lubricating oil composition comprising a major amount of an oil of lubricating viscosity and a minor amount, ef- fective to inhibit the accumulation of black sludge in a gasoline fueled internal combustion engine, of an aliphatic hydro- carbon substituted aromatic hydrocarbon. The aliphatic hydrocarbon substituted aromatic hydrocarbon comprises a com- pound of the formula Ar-R-(Ar)_n, wherein each Ar is independently an aromatic nucleus having from 0 to 3 substituents, R is a hydrocarbyl group, and n is an integer ranging from 1 to about 6. In a further embodiment, the aliphatic hydrocar- bon substituted aromatic hydrocarbon further comprises from about 1 to about 50 percent by weight of tetrahydronaph- thalene or hydrocarbyl substituted tetrahydronaphthalenes.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

-1-

ALIPHATIC HYDROCARBON SUBSTITUTED AROMATIC
HYDROCARBONS TO CONTROL BLACK SLUDGE IN LUBRICANTS

FIELD OF THE INVENTION

5 This invention relates to a method for controlling deposit formation and accumulation of deposits on parts of a gasoline fueled internal combustion engine which are exposed to lubricating oil. In particular, it relates to a method for controlling a new type of deposit referred to
10 as "black sludge" by lubricating the internal combustion engine with a lubricating oil which has incorporated therein an effective amount of certain aliphatic hydrocarbon substituted aromatic hydrocarbons.

BACKGROUND OF THE INVENTION

15 Over the years deposit formation in internal combustion engines has been a continuing problem. The amount of deposit formation had been controlled to some extent by the use of antioxidants and metal salts, particularly highly basic metal salts, of various organic
20 acids. While these efforts provided some benefit, a particularly troublesome type of deposit referred to as "sludge" continued to form in internal combustion engines. This sludge accumulated on the various internal parts of the engine and caused sluggish operation, increased wear
25 and sometimes resulted in blocked oil passages resulting in extensive wear and/or failure of the engine. The only way known to control accumulation of harmful amounts of

- 2 -

sludge was to change the engine oil at frequent intervals, usually every 30 days or every 1,000 miles of operation.

By the late 1950's and early 1960's, additives were developed which were found to control sludge formation. These additives, generally referred to as "ashless dispersants", and refinements thereof, revolutionized lubricant additive chemistry and resulted in the ability to extend oil change intervals to up to as long as one year or more.

Recently, and particularly in Europe, a new type of engine deposit has been observed. This deposit is sometimes referred to as "black sludge" or "German sludge" because it was first observed in Germany. Black sludge causes operational problems similar to those observed with the earlier observed sludge formation. Conventional engine oil additives, including the ashless dispersants, have not effectively controlled formation and/or accumulation of black sludge. Accordingly, a method for controlling the formation and/or accumulation of black sludge in an internal combustion engine would be of considerable value.

SUMMARY OF THE INVENTION

This invention provides lubricating oil compositions which provide a means for inhibiting or controlling the formation and accumulation of black sludge in gasoline fueled internal combustion engines. This is accomplished by incorporating into a lubricating oil composition which allows the accumulation of black sludge in a gasoline fueled internal combustion engine, a minor amount, effective to inhibit the formation or accumulation of black sludge in said engine, of an aliphatic hydrocarbon substituted aromatic hydrocarbon. The aliphatic hydrocarbon substituted aromatic hydrocarbon comprises a composition of the formula

- 3 -



wherein each Ar is independently an aromatic nucleus having from 0 to 3 substituents, R is a hydrocarbonyl group, and n is an integer ranging from 1 to about 6, with the proviso that n does not exceed the available valences of R. In a further embodiment, the aliphatic hydrocarbon substituted aromatic hydrocarbon further comprises from about 1 to about 50 percent, often from about 2 to about 25 percent by weight of tetrahydronaphthalene or hydrocarbonyl substituted tetrahydronaphthalenes. Also provided is a method for inhibiting the accumulation of black sludge in an internal combustion engine, which method comprises lubricating said internal combustion engine with a lubricating oil composition containing a minor amount effective to inhibit the accumulation of black sludge in said engine, of the above-described aliphatic hydrocarbon substituted aromatic hydrocarbon.

DETAILED DESCRIPTION OF THE INVENTION

As mentioned hereinabove, the present invention relates to improvements in lubricating oil compositions which otherwise allow the accumulation of black sludge in a gasoline fueled internal combustion engine. Gasoline fueled engines employ as the operating fuel automotive gasoline meeting the specifications given in American Society for Testing and Materials Specification D-439, "Standard Specification for Automotive Gasoline", which is expressly incorporated herein by reference.

Black Sludge

The formation and accumulation of black sludge in gasoline fueled engines, is a relatively recently observed phenomenon. Black sludge appears to be quite different from the sludge usually encountered in a gasoline fueled internal combustion engine, for example, that generated in the Sequence V-D test under low temperature operating

- 4 -

conditions. It is similar in appearance to the sludge formed in a diesel engine. Black sludge appears to occur mainly under high temperature oxidizing conditions. It is deposited primarily on the valve deck, rocker cover and other cooler engine parts. The deposits are often hard and resinous. Workers have suspected that it is possibly related to certain lubricant base stocks and/or fuels, although no definitive data is available at the present time. Black sludge accumulation has been observed primarily in gasoline fueled internal combustion engines used in the European market. It is unusual for such formations to appear in gasoline engines. Sludge usually found in a gasoline engine is lead sludge, sludge containing combustion by-products, and emulsion sludge which contains water and other products. The formation and/or accumulation of sludge, other than black sludge, in a gasoline engine is usually readily controlled by the use of ashless dispersants such as succinimide dispersants, ester dispersants, Mannich type dispersants and other ashless dispersants.

Black sludge appears to be quite different from the sludge usually encountered in a gasoline fueled engine. Black sludge is also sometimes referred to as nitrate sludge or high temperature sludge. It has been often observed that there is a high content of organic nitrates in used oil containing black sludge. As is well known, organic nitrates are formed in an engine during combustion of gasoline fuel with air. Nitrogen in the air forms nitrogen oxides (NO_x). A discussion of black sludge, including a description, photographs, theories regarding its formation and the like, appears in the house organ for German BP filling stations entitled "Tank Insel", Zeitschrift für BP Tankstellen, #6, November-December, 1986, pages 16-17. This publication indicates that solutions to the black sludge problem do exist, but only describes the solutions in terms of commercial brand name oils. A further discussion of black sludge appears in the

- 5 -

newsletter entitled "the LUBRIZOL NEWSLINETM", Vol 4, No 1, April, 1986. Each of the above-mentioned publications is expressly incorporated herein by reference.

Aliphatic Hydrocarbon Substituted Aromatic Hydrocarbon

5 Aliphatic hydrocarbon substituted aromatic
hydrocarbons useful in the compositions and methods of this invention are well known in the art. They can be represented by the formula



10 wherein each Ar is independently an aromatic nucleus having from 0 to 3 substituents, R is a hydrocarbyl group, and n is an integer ranging from 0 to about 6, with the proviso that n does not exceed the available valences of R. The aliphatic hydrocarbon substituted aromatic
15 hydrocarbon useful in this invention comprises a compound of formula (I) wherein n = 1 to 6.

Ar may be a single ring aromatic nucleus, such as a benzene ring, a polynuclear fused ring aromatic, such as naphthyl or a higher fused aromatic moiety or a linked
20 aromatic nucleus wherein two aromatic groups as described hereinabove are linked by a bridging linkage individually chosen from single bonds linking carbon atoms in the aromatic nuclei, lower alkylene linkages, ether linkages, sulfide or polysulfide linkages, lower alkylene ether
25 linkages, and the like. Examples of aromatic nuclei are described at length in U.S. 4,320,021, which patent is expressly incorporated herein by reference for relevant disclosures contained therein.

Substituents on Ar may be any group that does not
30 significantly detract from the essentially hydrocarbon nature of Ar. Such substituents may include, but are not necessarily limited to, hydrocarbyl, halo, lower hydrocarbyloxy, lower hydrocarbylthio, and the like. Preferred substituents are hydrocarbyl groups, especially
35 alkyl or alkenyl groups, having from about 6 to about 30

- 6 -

carbons. In a preferred embodiment, the aromatic group Ar is a benzene ring which may be unsubstituted or which may contain from 1 to 3 substituents, that is, it may contain from 0 to about 3 substituents. Often Ar has an average of from 0 to 1 substituents. The substituents referred to hereinabove do not include the substituent R in formula (I).

It is to be noted that when the term "hydrocarbyl" or "hydrocarbon" is used in describing a group or substituent in this specification and the appended claims, it is also intended to embrace substantially hydrocarbyl groups or substituents unless expressly stated otherwise. Such substantially hydrocarbyl groups or substituents are those which are substituted with non-hydrocarbyl groups which do not substantially affect the hydrocarbyl nature or character or the group or substituent in the context of the invention and which would, therefore, be considered to be within the scope of the terms "hydrocarbyl" or "hydrocarbon" by the skilled worker in the art. For example, it is obvious that, in the context of this invention, a C_{30} hydrocarbyl substituent and a C_{30} hydrocarbyl substituent substituted with a methylmercapto or methoxy group would be substantially similar in their properties with regard to their use in this invention, and would, in fact, be recognized as equivalents in the context of this invention by one of ordinary skill in the art.

In general, when such non-hydrocarbyl groups are present within a group or substituent or as a substituent on any such group or substituent, there will be no more than two such non-hydrocarbyl groups for each ten carbon atoms in the hydrocarbyl or hydrocarbon group or substituent; preferably not more than one for each ten carbon atoms. Generally, however, unless expressly stated otherwise, it is preferred that no such non-hydrocarbyl groups be present and that the hydrocarbyl or hydrocarbon groups or substituents be solely hydrocarbon in nature.

- 7 -

The Aliphatic Hydrocarbon Substituent

The aromatic hydrocarbon useful in the lubricating oil compositions and methods of this invention contain one or more aliphatic hydrocarbon substituents. When the aliphatic hydrocarbon substituted aromatic hydrocarbon comprises a single aromatic moiety, the aromatic moiety will be substituted by at least one aliphatic hydrocarbon substituent. That is, the aliphatic hydrocarbon substituted aromatic hydrocarbon will have the general formula



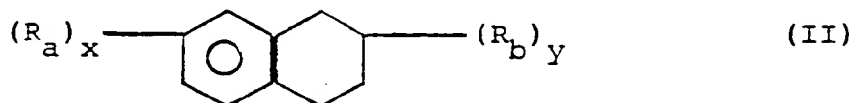
wherein Ar is as defined hereinabove, n is 0 and R is an aliphatic hydrocarbon group. In this case, R is preferably an alkyl or alkenyl group.

It is readily apparent that, depending on the value of n, R will be a mono- or poly-valent group. As mentioned hereinabove, when n is 0, R is an essentially mono-valent hydrocarbon substituent on Ar. As mentioned hereinabove, the aliphatic hydrocarbon substituted aromatic hydrocarbon comprises at least one percent by weight of a compound of formula (I) wherein n is an integer ranging from 1 to about 6 with the proviso that n does not exceed the available valences of R. Accordingly, when n is 1, R is a divalent group, when n is 2, R is a trivalent group and so on, provided that n does not exceed the available valences of R.

As discussed hereinabove for hydrocarbon or hydrocarbyl groups or substituents, R may contain non-hydrocarbyl substituents, provided that they do not detract from the essentially hydrocarbon or hydrocarbyl character of R. Preferably, R is a hydrocarbyl group containing from about 6 to about 30 carbons, more preferably about 8 to about 15 carbons.

- 8 -

In another embodiment, the aliphatic hydrocarbon substituted aromatic hydrocarbon may comprise or may be a composition having the formula



5 wherein each R_a and R_b is independently a hydrocarbyl group having from 1 to about 30 carbon atoms, x and y are each independently an integer from 0 to 4, preferably 1 to 3, more preferably 1 to 2. These compounds are referred to as tetrahydronaphthalene, hydrocarbyl substituted
10 tetrahydronaphthalenes or tetralins.

The aliphatic hydrocarbon substituted aromatic hydrocarbon may comprise a mixture of two or more of the above-discussed components. That is, the aliphatic hydrocarbon substituted aromatic hydrocarbon may contain
15 mixtures of materials of formula



and may contain compounds of formula (II). For example, the aliphatic hydrocarbon substituted aromatic hydrocarbon may be a mixture of components of Formula (I) wherein the
20 various components each have similar Ar groups, but n may be 0 or 1, but at least one percent by weight will be a compound of formula (I) wherein n is at least 1, and R will, depending on n , be an alkyl or alkylene group having, for example, 8 to about 14 carbon atoms.

25 In general, the aliphatic hydrocarbon substituted aromatic hydrocarbon comprises from about 1 to about 75 percent, preferably from about 5 percent to about 50 percent by weight of a composition of formula



30 wherein each Ar is independently an aromatic nucleus having from 0 to 3 substituents, R is a hydrocarbyl group,

- 9 -

and n is an integer ranging from 1 to about 6, with the proviso that n does not exceed the available valences of R.

As mentioned hereinabove, the aliphatic hydrocarbon substituted aromatic hydrocarbon may comprise a component having the formula (II). In a more likely situation, the aliphatic hydrocarbon substituted aromatic hydrocarbon may comprise from about 1 percent to about 50 percent, preferably from about 2 percent to about 20 percent by weight of tetrahydronaphthalene or hydrocarbyl substituted tetrahydronaphthalenes.

Frequently, the aliphatic hydrocarbon substituted aromatic hydrocarbon will comprise a mixture of various types of the above-described components.

In an especially preferred embodiment, the aliphatic substituted aromatic hydrocarbon comprises a composition wherein at least one Ar in Formula I is a benzene ring having from 0 to about 3 substituents, wherein the substituents are as defined hereinabove. Particularly preferred is when the aliphatic hydrocarbon substituted aromatic hydrocarbon contains at least 10 percent by weight, more preferably at least 25 percent by weight of a compound of formula (I) where n is 1 or 2, most preferably 1.

25 Sources of Aliphatic Hydrocarbon Substituted Aromatic Hydrocarbon

Aliphatic hydrocarbon substituted aromatic hydrocarbons useful in the compositions and methods of this invention are well known in the art and can be prepared by alkylation of aromatic compounds such as benzene, toluene, naphthalene, anthracene and the like. Generally, the aliphatic hydrocarbon substituted aromatic hydrocarbons can be prepared by alkylation of aromatic compounds with halogenated aliphatic hydrocarbons or with olefins. Procedures for preparing such compositions are well known and are described in the following patents and publications:

- 10 -

Kirk and Othmer, "Encyclopedia of Chemical Technology", Third Edition, Volume II, "Alkylation", pages 50-51, 58-65, John Wiley and Sons (1978)

5 US 1,815,022
US 1,878,262
US 1,963,917
US 1,963,918
US 2,015,748
US 2,030,307
10 US 2,475,970
US 2,688,643
US 2,810,769
US 2,882,289
US 3,104,267
15 US 3,316,294
US 3,775,325

West German Application 3,440,196

In a preferred embodiment of this invention, the aliphatic hydrocarbon substituted aromatic hydrocarbon
20 comprises from about 20 to about 50 percent by weight, but may comprise as little as 1 percent by weight or up to 100 percent by weight, of a compound of the formula



wherein each Ar is independently an aromatic nucleus
25 having from 0 to 3 substituents, R is a hydrocarbonyl group, and n is an integer ranging from 1 to about 6, with the proviso that n does not exceed the available valences of R. Commercially available products contain a wide range of compounds of formula (I). Several contain from about
30 10 to about 20 percent by weight, another contains about 36 percent by weight of the aliphatic hydrocarbon substituted aromatic composition wherein n is an integer from 1 to 6. Usually n equals 1. These compounds are obtained in varying amounts depending on reaction

- 11 -

conditions. These preferred compounds are obtained when the alkylating agent is or contains a di- or polyfunctional compound such as a di- or polychlorinated wax. As discussed in several of the above references, the amount of such compounds obtained during an alkylation process depends on numerous factors including, but not limited to, the amount of di- and polyhalogenated reactant, relative amounts of reactants and the like.

Tetrahydronaphthalene and alkylated versions thereof can also be formed during the alkylation of aromatic compounds.

Many materials useful in the compositions and methods of this invention are commercially available. Examples include detergent alkylates from numerous sources, Wibarco Heavy Alkylate (Chemische Fabrik Wibarco GmbH, West Germany) and Vista 3050 specialty alkylate (Vista Chemical Company, Baltimore, Maryland).

The Oil of Lubricating Viscosity

The lubricating compositions and methods of this invention employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof.

Natural oils include animal oils and vegetable oils (e.g. castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils, alkylated diphenyl ethers and alkylated diphenyl sulfides.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils that can be used.

- 12 -

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids with a variety of alcohols (e.g., butyl alcohol, dodecyl alcohol, ethylene glycol, diethylene glycol monoether, etc.).

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans and the like.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, hydrotreating, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

Specific examples of the above-described oils of lubricating viscosity are given in Chamberlin III, U.S. 4,326,972 and European Patent Publication 107,282, both of which are hereby incorporated by reference for relevant disclosures contained therein.

- 13 -

A basic, brief description of lubricant base oils appears in an article by D. V. Brock, "Lubrication Engineering", Volume 43, pages 184-5, March, 1987, which article is expressly incorporated by reference for
5 relevant disclosures contained therein.

Other Additives

The compositions of this invention may contain other components. The use of such additives is optional and the presence thereof in the compositions of this invention
10 will depend on the particular use and level of performance required. The compositions may comprise a zinc salt of a dithiophosphoric acid. Zinc salts of dithiophosphoric acids are often referred to as zinc dithiophosphates, zinc 0,0-dihydrocarbyl dithiophosphates, and other commonly
15 used names. They are sometimes referred to by the abbreviation ZDP. One or more zinc salts of dithiophosphoric acids may be present in a minor amount to provide additional extreme pressure, anti-wear and anti-oxidancy performance.

20 In addition to zinc salts of dithiophosphoric acids discussed hereinabove, other additives that may be used in the lubricating oils of this invention include, for example, detergents, dispersants, oxidation inhibiting agents, pour point depressing agents, extreme pressure
25 agents, anti-wear agents, color stabilizers and anti-foam agents.

Auxiliary extreme pressure agents and corrosion and oxidation inhibiting agents which may be included in the compositions of the invention are exemplified by chlori-
30 nated aliphatic hydrocarbons such as chlorinated wax, organic sulfides and polysulfides such as benzyldisulfide, bis(chlorobenzyl)disulfide, dibutyltetrasulfide, and sulfurized alkylphenol. Also contemplated are phosphorus esters.

35 Viscosity improvers (also sometimes referred to as viscosity index improvers) are additives which improve the viscosity-temperature characteristics of oils. Such

- 14 -

additives are often included in the compositions of this invention. Viscosity improvers are usually polymers, including polymethacrylic acid esters, diene polymers, polyalkyl styrenes, alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers which also have dispersant and/or antioxidancy properties are known. Such products are described in numerous publications including Dieter Klamann, "Lubricants and Related Products", Verlag Chemie GmbH (1984), pp 185-193; C. V. Smalheer and R. K. Smith, "Lubricant Additives", Lezius-Hiles Co (1967); M. W. Ranney, "Lubricant Additives", Noyes Data Corp. (1973), pp 92-145; M. W. Ranney, "Lubricant Additives, Recent Developments", Noyes Data Corp (1978), pp 139-164; and M. W. Ranney, "Synthetic Oils and Additives for Lubricants", Noyes Data Corp. (1980), pp 96-166. Each of these publications is hereby expressly incorporated by reference.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants and oil-based compositions to improve low temperature properties of oil-based compositions is well known in the art. See for example, page 8 of "Lubricant Additives" by C. V. Smallheer and R. Kennedy Smith (Lezius-Hiles Company Publishers, Cleveland, Ohio, 1967). Pour point depressants useful for the purpose of this invention, techniques for their preparation and their use are described in U.S. Patent numbers 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,748; 2,721,877; 2,721,878; and 3,250,715 which are expressly incorporated by reference for their relevant disclosures.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicone or organic polymers. Additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation,

- 15 -

1976), pages 125-162, which is expressly incorporated herein by reference.

5 Detergents and dispersants may be of the ash-producing or ashless type. The ash-producing detergents are exemplified by oil soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage.

10 The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. Basic salts and techniques for preparing and using them are well known to those skilled in the art and need not be discussed in
15 detail here.

Ashless detergents and dispersants are so-called despite the fact that, depending on its constitution, the detergent or dispersant may upon combustion yield a non-volatile residue such as boric oxide or phosphorus
20 pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

25 (1) Reaction products of carboxylic acids (or derivatives thereof) containing at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic
30 inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent number 1,306,529 and in many U.S. patents including the following which are expressly incorporated herein by reference.

- 16 -

	3,163,603	3,351,552	3,541,678
	3,172,892	3,381,022	3,542,680
	3,184,474	3,399,141	3,567,637
	3,215,707	3,415,750	3,574,101
5	3,219,666	3,433,744	3,576,743
	3,271,310	3,444,170	3,630,904
	3,272,746	3,448,048	3,632,510
	3,281,357	3,448,049	3,632,511
	3,306,908	3,451,933	3,697,428
10	3,311,558	3,454,607	3,725,441
	3,316,177	3,467,668	4,194,886
	3,340,281	3,501,405	4,234,435
	3,341,542	3,522,179	4,491,527
	3,346,493	3,541,012	RE 26,433
15			

The reaction products include amides, imides, amine and metal salts, esters, acids and mixtures thereof, including mixtures of discrete molecules of two or more of the types mentioned above, or mixtures wherein a single molecule contains various combinations of the above-described chemical types.

Of the above-described reaction products of carboxylic acids, certain members are preferred. The preferred product is that obtained by reaction of a carboxylic acid containing at least about 34, and preferably at least about 54 carbon atoms with an ethylene polyamine to form a nitrogen-containing product. Especially preferred is the reaction product of an alkenyl substituted succinic anhydride meeting the above requirements, with an ethylene polyamine (including cyclic nitrogen reactants such as piperazines). This reaction results in a mixture containing varying amounts, depending on reaction conditions, of amide, imide, amine salt, amide-salts, amide-acids, and various combinations thereof. Useful nitrogen-containing products may be

- 17 -

obtained by post-treatment of esters, metal salts, residual-free acid, etc., with the above-described ethylene polyamine. A wide variety of the preferred nitrogen-containing product useful in the compositions of this invention are described in U.S. Patents 3,272,746; 3,216,666; 3,172,892; 4,234,435; and numerous others.

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably polyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. patents:

3,275,554

3,454,555

3,438,757

3,565,804

(3) Reaction products of alkyl phenols in which the alkyl groups contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. patents are illustrative:

20

3,413,347

3,725,480

3,697,574

3,726,882

3,725,277

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. patents:

- 18 -

	3,036,003	3,282,955	3,493,520	3,639,242
	3,087,936	3,312,619	3,502,677	3,649,229
	3,200,107	3,366,569	3,513,093	3,649,659
	3,216,936	3,367,943	3,533,945	3,658,836
5	3,254,025	3,373,111	3,539,633	3,697,574
	3,256,185	3,403,102	3,573,010	3,702,757
	3,278,550	3,442,808	3,579,450	3,703,536
	3,280,234	3,455,831	3,591,598	3,704,308
	3,281,428	3,455,832	3,600,372	3,708,522
10				4,234,435

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. patents:

	3,329,658	3,666,730
	3,449,250	3,687,849
20	3,519,565	3,702,300

The above-noted patents are incorporated herein by reference for their disclosures of ashless dispersants.

When the above-described ashless dispersants of this invention are employed in the lubricating compositions of this invention, they can be used in amounts ranging from about 0.01 to about 50 percent by weight of the lubricating oil composition. More often, they are used in amounts ranging from about 0.5 to about 25 percent, preferably from about 0.5 to about 10 percent by weight. Most preferably, they comprise about 0.5 to about 5 percent by weight of the lubricating oil composition. Dispersants containing the succinimide group are especially preferred.

- 19 -

Other members of above-illustrated group of optional additives may each be present in lubricating compositions at a concentration of as little as 0.001 percent by weight usually ranging from about 0.01 percent to about 20 percent by weight. In most instances, they each may be present from about 0.1% to about 10% by weight.

The various additives described herein can be added directly to the lubricant. Preferably, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually comprise about 0.1 to about 80% by weight of the compositions of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove. Concentrations such as 15%, 20%, 30% or 50% or higher may be employed. These concentrates are then added to lubricating oils at levels adequate to provide the required degree of performance.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

The aliphatic hydrocarbon substituted aromatic hydrocarbon described herein is used in a minor amount with a major amount of an oil of lubricating viscosity to prepare the lubricating oils of this invention. A minor amount is less than 50 percent by weight of the total composition, whereas a major amount is more than 50 percent by weight of the composition. Thus, for example, 5, 10, 30 or 40 percent are minor amounts, while 51, 60, 70, 90, etc. percent are major amounts. The aliphatic hydrocarbon substituted aromatic hydrocarbons of this invention are generally used at levels from about 5 to 35 percent by weight, more often from about 5 to 10 percent

- 20 -

by weight of the total composition. Thus, depending on the precise makeup of the aliphatic hydrocarbon substituted aromatic hydrocarbon, varying amounts of compounds of formula (I), wherein n is an integer between 1 and 6 and/or compounds of formula (II) are provided.

Compounds of formula I, wherein n is an integer between 1 and 6, more preferably 1, are often present in concentrations ranging from about 1 to about 15 percent by weight, more preferably 2 to about 10 percent by weight. Most often these compounds are present in concentrations ranging between about 3 to about 5 percent by weight, all percentages being based on the total weight of the lubricating oil composition.

The lubricating compositions of this invention are illustrated by the examples in the following Table I. The lubricating compositions are prepared by combining the specified ingredients, individually or from concentrates, in the indicated amounts and oil of lubricating viscosity to make the total 100 parts by weight. All parts and percentages are by weight of the total composition unless otherwise indicated. Unless indicated otherwise, the amount of each listed additive is that of the neat additive, free of oil or other diluent. These examples are presented for illustrative purposes only, and are not intended to limit the scope of this invention.

TABLE I
Lubricant Examples

	<u>1</u>	<u>2</u>	<u>3</u>
5			
Ashless dispersants derived from polyisobutenyl succinic anhydride	4.13	3.34	1.88
Metal salts of organic acids	1.27	1.40	1.03
Zinc salt of dihydrocarbon substituted dithiophosphoric acids	1.34	1.01	1.23
10			
Basic calcium salt of sulfurized alkyl phenols	0.2	0.81	0.46
Sulfurized Diels-Alder adduct	0.16	0.20	
Alkylated aryl amine		0.17	0.17
15			
Neutral calcium sulfonate		0.2	
Fatty amide mixture	14 ppm	15 ppm	10 ppm
Silicone antifoam	1.07	1.6	1.44
Hydrogenated styrene-butadiene copolymer		0.5	
20			
Commercial acrylate/methacrylate pour depressants			

TABLE I Continued)

	<u>1</u>	<u>2</u>	<u>3</u>
5 Styrene/maleate copolymer-amine reaction product	0.08		0.08
Mineral oil	61.82	77.7	86.15
Synthetic (polyalphaolefin) oil	24.3		
Aliphatic hydrocarbon substituted aromatic*	5.63	8.4	7.56

*: Heavy Alkylate - typical composition (parts by weight)

- 10 10% linear alkyl benzene
50% diphenyl alkane
30% dialkyl benzene
10% oligoalkyl benzene

- 23 -

These lubricating oil compositions and similarly formulated lubricating oil compositions that did not contain the aliphatic hydrocarbon substituted aromatic hydrocarbon described herein were evaluated with respect to their ability to inhibit or to reduce the accumulation of black sludge in an internal combustion engine. Evaluations were conducted using modified Daimler-Benz M-102-E tests. The test engine is a gasoline fueled four cylinder, four-stroke, 2.3 liter fuel injected engine. In each case, the composition containing the aliphatic hydrocarbon substituted aromatic hydrocarbons of this invention was found to be superior to a comparable oil composition that did not contain aliphatic hydrocarbon substituted aromatic hydrocarbons described herein.

The following Table II illustrates the superior performance of lubricating oil compositions of this invention compared to similar lubricating oil compositions which did not contain the heavy alkylate containing diphenylalkane (the compound of Formula I where $n = 1$). The numerical rating system is from 1 to 10, where 10 indicates an engine free of black sludge. The higher the numerical rating, the better the performance of the lubricant with respect to inhibiting the formation and/or accumulation of black sludge.

The compositions containing diphenylalkane are those of Table I, items 1, 2 and 3. Compositions A, B and C in Table II are similar to items 1, 2 and 3 respectively except that A, B and C do not contain heavy alkylate comprising diphenylalkane.

Lubricant set 1 and A, and set 2 and B were exposed to essentially the same test conditions except for test duration. Test duration for each lubricant set is shown in Table II. Lubricant set 3 and C was run under conditions more severe than those for set 1 and A.

- 24 -

TABLE II

2	Lubricating Oil		
3	<u>Composition</u>	<u>Test Duration hours</u>	<u>Results (Rating)</u>
4	1	150	9.7
5	A	150	9.4
6	2	225	8.1
7	B	225	7.4
8	3	150	8.9
9	C	150	7.8

10 The numerical ratings for compositions 1, 2 and 3
11 indicate a "Pass" result with respect to inhibition of
12 black sludge formation and/or accumulation. The
13 numerical ratings for compositions A, B and C are
14 indicative of a "Fail" result.

$$9 \quad \text{Ar-R-(Ar)}_n \quad (\text{I})$$

1 2. In the lubricating oil composition of claim 1
2 wherein the aliphatic hydrocarbon substituted aromatic
3 hydrocarbon further comprises from about 1 to about 50
4 percent by weight of tetrahydronaphthalene or hydrocarbyl
5 substituted tetrahydronaphthalenes.

1 4. In the lubricating oil composition of claim 1
2 wherein n is 1 or 2.

1 5. In the lubricating oil composition according to
2 claim 1 wherein R contains from about 6 to about 30 carbon
3 atoms.

- 26 -

1 6. In the lubricating oil composition according to
2 claim 1 wherein each substituent is independently a
3 hydrocarbonyl based group having from about 6 to about 30
4 carbon atoms.

1 7. In the lubricating oil composition according to
2 claim 5 wherein the aromatic nucleus is a benzene ring and
3 n equals 1 or 2.

1 8. In the lubricating composition according to
2 claim 7, which further comprises from about 0.5 to about
3 10 percent by weight of the reaction product of an alkyl
4 or alkenyl substituted succinic anhydride or derivative
5 thereof, wherein the alkyl or alkenyl group contains at
6 least about 30 carbon atoms, with an ethylene polyamine.

1 9. A lubricating oil composition comprising a major
2 amount of an oil of lubricating viscosity and a minor
3 amount, effective to inhibit the accumulation of black
4 sludge in a gasoline fueled internal combustion engine, of
5 an aliphatic hydrocarbon substituted aromatic hydrocarbon
6 which comprises a composition of the formula

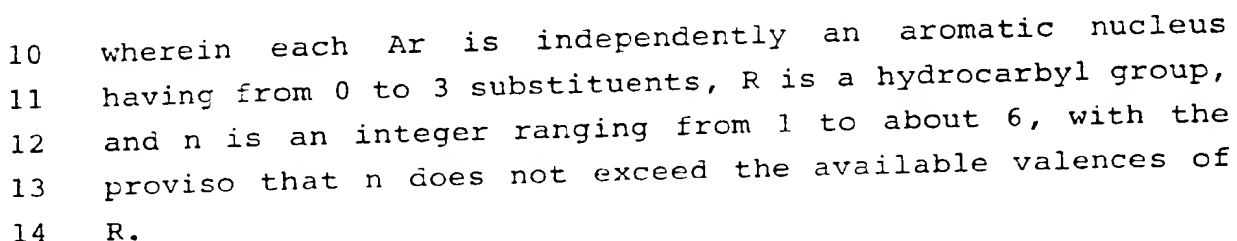


8 wherein each Ar is independently an aromatic nucleus
9 having from 0 to 3 substituents, R is a hydrocarbonyl group,
10 and n is an integer ranging from 1 to about 6, with the
11 proviso that n does not exceed the available valences of
12 R.

1 10. The lubricating oil composition according to
2 claim 9 wherein the aliphatic hydrocarbon substituted
3 aromatic hydrocarbon comprises from about 1 percent to
4 about 50 percent by weight of tetrahydronaphthalene or
5 hydrocarbonyl substituted tetrahydronaphthalenes.

1 13. The lubricating oil composition according to
2 claim 11 wherein the aromatic nucleus is a benzene ring
3 and n equals 1 or 2.

1 15. A method for inhibiting the accumulation of
2 black sludge in a gasoline fueled internal combustion
3 engine, which method comprises lubricating said internal
4 combustion engine with a lubricating oil composition
5 comprising a minor amount, effective to inhibit the
6 accumulation of black sludge in said engine, of an
7 aliphatic hydrocarbon substituted aromatic hydrocarbon
8 which comprises a composition of the formula



- 28 -

1 16. The method of claim 15 wherein the aliphatic
2 hydrocarbon substituted aromatic hydrocarbon comprises
3 from about 1 to about 50 percent by weight of
4 tetrahydronaphthalene or hydrocarbyl substituted
5 tetrahydronaphthalenes.

1 17. The method according to claim 15 wherein R
2 contains from about 6 to about 30 carbon atoms.

1 18. The method according to claim 17 wherein the
2 aromatic nucleus is a benzene ring and n equals 1 or 2.

1 19. The method according to claim 15 wherein the
2 lubricating oil composition further comprises about 0.5 to
3 about 10 percent by weight of the reaction product of an
4 alkyl or alkenyl substituted succinic anhydride or
5 derivative thereof, wherein the alkyl or alkenyl group
6 contains at least about 30 carbon atoms, with an ethylene
7 polyamine.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 88/02045

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC C 10 M 127/06; ⁴ C 10 M 161/00; //(C 10 M 161/00, 127:04, 127:06, 133:52, IPC: 143:12, 143:10); C 10 N 30:04, 40:00																																
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: none; padding: 10px;">IPC⁴</td> <td style="border: none; padding: 10px;">C 10 M</td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 10px;"> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸ </div>			Classification System	Classification Symbols	IPC ⁴	C 10 M																										
Classification System	Classification Symbols																															
IPC ⁴	C 10 M																															
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <thead> <tr> <th style="width: 10%;">Category ⁹</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>FR, A, 2130005 (ESSO STANDARD) 3 November 1972, see page 2, line 21 - page 4, line 30; claims 1-4, 6-8</td> <td style="vertical-align: top;">1, 3, 4, 5, 6, 7, 9, 11, 13, 17, 18</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="text-align: center;">--</td> <td style="vertical-align: top;">2, 8, 10, 12, 14, 16, 19</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>GB, A, 475040 (F. NEUKOM) 9 December 1937, see column 1, lines 9-18, 40-50; example 1; claims 1, 2, 4</td> <td style="vertical-align: top;">2, 10, 16</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="text-align: center;">--</td> <td style="vertical-align: top;">8, 12, 14, 19</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>FR, A, 2348962 (EXXON RESEARCH AND ENGINEERING CO.) 18 November 1977, see page 2, line 34 - page 3, line 27; page 9, line 17 - page 10, line 11; page 13, lines 18-32; claims 1, 5, 6</td> <td style="vertical-align: top;">8, 12, 14, 19</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="text-align: center;">--</td> <td style="vertical-align: top;">1, 2, 3, 4, 9, 10, 15, 16</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>DE, C, 920319 (DEUTSCHE SHELL AG) 18 November 1954, see page 2, line 124 - page 3, line 3; page 3, lines 37-48; example 3; claims 1, 3, 7</td> <td style="vertical-align: top;">1, 2, 3, 4, 9, 10, 15, 16</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">P, X</td> <td style="text-align: center;">--</td> <td style="vertical-align: top;">1, 3, 4, 6, 9, 15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">P, X</td> <td>WO, A, 87/04180 (THE LUBRIZOL CORP.) 16 July 1987, see page 5, lines 1-24; ./. </td> <td style="vertical-align: top;">1, 3, 4, 6, 9, 15</td> </tr> </tbody> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	FR, A, 2130005 (ESSO STANDARD) 3 November 1972, see page 2, line 21 - page 4, line 30; claims 1-4, 6-8	1, 3, 4, 5, 6, 7, 9, 11, 13, 17, 18	Y	--	2, 8, 10, 12, 14, 16, 19	Y	GB, A, 475040 (F. NEUKOM) 9 December 1937, see column 1, lines 9-18, 40-50; example 1; claims 1, 2, 4	2, 10, 16	Y	--	8, 12, 14, 19	Y	FR, A, 2348962 (EXXON RESEARCH AND ENGINEERING CO.) 18 November 1977, see page 2, line 34 - page 3, line 27; page 9, line 17 - page 10, line 11; page 13, lines 18-32; claims 1, 5, 6	8, 12, 14, 19	X	--	1, 2, 3, 4, 9, 10, 15, 16	X	DE, C, 920319 (DEUTSCHE SHELL AG) 18 November 1954, see page 2, line 124 - page 3, line 3; page 3, lines 37-48; example 3; claims 1, 3, 7	1, 2, 3, 4, 9, 10, 15, 16	P, X	--	1, 3, 4, 6, 9, 15	P, X	WO, A, 87/04180 (THE LUBRIZOL CORP.) 16 July 1987, see page 5, lines 1-24; ./.	1, 3, 4, 6, 9, 15
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³																														
X	FR, A, 2130005 (ESSO STANDARD) 3 November 1972, see page 2, line 21 - page 4, line 30; claims 1-4, 6-8	1, 3, 4, 5, 6, 7, 9, 11, 13, 17, 18																														
Y	--	2, 8, 10, 12, 14, 16, 19																														
Y	GB, A, 475040 (F. NEUKOM) 9 December 1937, see column 1, lines 9-18, 40-50; example 1; claims 1, 2, 4	2, 10, 16																														
Y	--	8, 12, 14, 19																														
Y	FR, A, 2348962 (EXXON RESEARCH AND ENGINEERING CO.) 18 November 1977, see page 2, line 34 - page 3, line 27; page 9, line 17 - page 10, line 11; page 13, lines 18-32; claims 1, 5, 6	8, 12, 14, 19																														
X	--	1, 2, 3, 4, 9, 10, 15, 16																														
X	DE, C, 920319 (DEUTSCHE SHELL AG) 18 November 1954, see page 2, line 124 - page 3, line 3; page 3, lines 37-48; example 3; claims 1, 3, 7	1, 2, 3, 4, 9, 10, 15, 16																														
P, X	--	1, 3, 4, 6, 9, 15																														
P, X	WO, A, 87/04180 (THE LUBRIZOL CORP.) 16 July 1987, see page 5, lines 1-24; ./.	1, 3, 4, 6, 9, 15																														
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																																
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">3rd October 1988</div> </td> <td style="width: 50%; border: none; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">27. 10. 88</div> </td> </tr> <tr> <td style="border: none; vertical-align: top;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: center;"> P.C.G. VAN DER PUTTEN </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">3rd October 1988</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">27. 10. 88</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;"> P.C.G. VAN DER PUTTEN </div>																										
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">3rd October 1988</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">27. 10. 88</div>																															
International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;"> P.C.G. VAN DER PUTTEN </div>																															

International Application No. PCT/US 88/02045

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
	page 6, line 3 - page 7, line 17; page 10, line 25 - page 11, line 7; claims 1,2,4	
	--	
A	US, A, 3057801 (D.R. WILGUS) 9 October 1962, see column 1, line 40 - column 2, line 26; column 5, lines 40-52; claims 1-5	1,3-5,7,9, 11,13,15,17, 18

Form PCT ISA 210 (extra sheet) (January 1985)

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8802045
SA 23293

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/10/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2130005	03-11-72	None	
GB-A- 475040		NL-C- 77687	
FR-A- 2348962	18-11-77	DE-A- 2716390	10-11-77
		US-A- 4073737	14-02-78
		JP-A- 52127905	27-10-77
		GB-A- 1585413	04-03-81
DE-C- 920319		None	
WO-A- 8704180	16-07-87	AU-A- 6833587	28-07-87
		EP-A- 0252947	20-01-88
		US-A- 4753745	28-06-88
		JP-T- 63502111	18-08-88
US-A- 3057801		GB-A- 924598	
		US-A- 2999120	